

PATENT SPECIFICATION
NO DRAWINGS



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Date of Application and filing Complete Specification: July 25, 1957.

No. 26343/57.

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Index at acceptance:—Class 140, A(2N3:2P:5G4:10B3).

International Classification:—B29d.

COMPLETE SPECIFICATION

**Method of Bonding Synthetic High Polymers to Polyurethane
Elastomers**

We, THE GENERAL TIRE & RUBBER COMPANY, of No. 1708 Englewood Avenue, Akron, County of Summit, State of Ohio, United States of America, a corporation organized under the laws of the State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the bonding of textile fabrics, filament cords and the like to vulcanized polyurethane elastomer structures; it also relates to the resulting composite articles. More particularly this invention relates to methods of bonding synthetic linear high polymers such as polyamide or polyester filaments having a high melting point to flexible elastomers of polyurethanes.

Elastomers have excep-

phthalate to a saturated polyurethane elastomer by forming on the cords a coating of an infusible insoluble resinous condensation product of an organic aldehyde and a polyhydric phenol and thereafter applying the elastomer under pressure to the cords. 45

Useful polyurethane elastomers are generally those which are flexible, generally linear, long chain reaction products of a polyglycol and a polyisocyanate. Generally the polyglycols used are linear polyesters of polyethers. Also, in order to provide polyesters of linear rubbery polymers of the solid non-porous type, the low acid number linear polyesters and polyethers are desirable. Polyesters with acid numbers of less than one give products which are superior, although we can, in accordance with the present invention, use polyesters with a much higher acid number, even to the range of an acid number of 60. The molecular weight of the polyesters should, for the preparation of 50

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60

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600

ERRATUM

SPECIFICATION No. 833,075

Page 1, in the heading, for "No. 26343/57" read "No. 23643/57"

THE PATENT OFFICE

3rd July 1961

to polymerize a serious obstacle to the use of polyurethane rubber in tyres.

The present invention provides a method by which a high degree of adhesion can be obtained between fabrics of the above-mentioned synthetic fibres and polyurethane rubbers, which are reaction products of a linear polyol with a diisocyanate, whereby tyres of superior quality can be produced.

Accordingly, in the manufacture of tyres, the present invention comprises a process of bonding tyre cords of nylon or of polyethylene ter-

useful polyester is one formed from the reaction of 6.7 mols of ethylene glycol, 3.3 mols of propylene glycol and 8.4 mols of adipic acid. The polyester preferably has a molecular weight of about 2000, an acid number under one and a viscosity of 500 cps at 73°C. 75

A

80

The polyethers used for preparing the improved polyurethane compounds have a molecular weight of at least 600 and preferably more; if materials rubbery at normal temperatures are desired, molecular weight of over

85

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COMPLETE SPECIFICATION

'Method of Bonding Synthetic High Polymers to Polyurethane Elastomers'

We, THE GENERAL TIRE & RUBBER COMPANY, of No. 1708 Englewood Avenue, Akron, County of Summit, State of Ohio, United States of America, a corporation organized under the laws of the State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the bonding of textile fabrics, filament cords and the like to vulcanized polyurethane elastomer structures; it also relates to the resulting composite articles. More particularly this invention relates to methods of bonding synthetic linear high polymers such as polyamide or polyester filaments having a high melting point to flexible elastomers of polyurethanes.

Because polyurethane elastomers have exceptional properties such as high abrasion resistance, high resistance to tearing, high tensile strength, high flex life and general ability to perform at elevated temperature, they are desirable for use in making tyres, belts and the like. A strong adhesion between the tyre cords and rubber is necessary to provide a satisfactory tyre.

The poor adhesion of polyurethane rubber to the synthetic fibres, nylon and polyesters, such as polyethylene terephthalate fibres has been a serious obstacle to the use of polyurethane rubber in tyres.

The present invention provides a method by which a high degree of adhesion can be obtained between fabrics of the above-mentioned synthetic fibres and polyurethane rubbers, which are reaction products of a linear polyol with a diisocyanate, whereby tyres of superior quality can be produced.

Accordingly, in the manufacture of tyres, the present invention comprises a process of bonding tyre cords of nylon or of polyethylene ter-

pthalate to a saturated polyurethane elastomer by forming on the cords a coating of an infusible insoluble resinous condensation product of an organic aldehyde and a polyhydric phenol and thereafter applying the elastomer under pressure to the cords.

Useful polyurethane elastomers are generally those which are flexible, generally linear, long chain reaction products of a polyglycol and a polyisocyanate. Generally the polyglycols used are linear polyesters of polyethers. Also, in order to provide polyesters of linear rubbery polymers of the solid non-porous type, the low acid number linear polyesters and polyethers are desirable. Polyesters with acid numbers of less than one give products which are superior, although we can, in accordance with the present invention, use polyesters with a much higher acid number, even to the range of an acid number of 60. The molecular weight of the polyesters should, for the preparation of rubbery polyurethane polymers, be above 500 and preferably above 1000. The maximum molecular weight of the polyester is dependent only upon the ability to economically make the polyesters of higher molecular weights, the higher molecular weights being preferred. Generally, it is exceedingly difficult to obtain polyesters with a molecular weight much above 3000 or 4000 without substantially higher costs.

Suitable polyesters are those containing methylene, ethylene and propylene groups. A useful polyester is one formed from the reaction of 6.7 mols of ethylene glycol, 3.3 mols of propylene glycol and 8.4 mols of adipic acid. The polyester preferably has a molecular weight of about 2000, an acid number under one and a viscosity of 500 cps at 73°C.

The polyethers used for preparing the improved polyurethane compounds have a molecular weight of at least 600 and preferably more; if materials rubbery at normal temperatures are desired, molecular weight of over

1000 are preferred. When the molecular weight of the polyether used for reacting with the isocyanates is less than 500 or 600, the product, while plastic, is too rigid for application as rubbery base materials at ordinary temperatures.

More rigid polyurethanes may be produced by increasing the amount of crosslinking in the resulting polyurethane, for instance, by using a crosslinking agent, such as trimethylol propane or by using polyesters or polyethers of the crosslinking type.

The preferred polyethers for polyurethane elastomers are mixed poly(ethylene-propylene) ether glycols, and polytetramethylene ether glycol. Desirable properties for the polyethers are active methylene groups, a very low acid number or no acid number and hydroxyl groups on the ends of the molecular chain.

Examples of suitable polyethers are from the class of polyalkylene ether glycols, such as polyethylene ether glycol, such as "Carbowax," having a molecular weight of about 1000, polytetramethylene ether glycol, polytrimethylene ether glycol, polyneopentylene ether glycol, polypentamethyl ether glycol, preferably having a molecular weight of above 600 and preferably of about 2000 to 4000 and mixed polyalkylene ether glycols such as poly(ethylene-propylene) ether glycols.

Any readily reactive organic diisocyanate having two and only two readily reactive isocyanate groups may be used for reacting with the polyester or polyether, but those having both isocyanate groups of about equal reactivity are preferred for at least part of the total isocyanate present to facilitate growth of the polyurethane chains. Tri-functional isocyanates like tri-functional polyesters act as cross-linking agents and are undesirable in appreciable quantity unless one of the functional groups is relatively non-reactive.

Various diisocyanates are commercially available and the following is a partial list:

- 1) Toluylene-2,4-diisocyanate
- 2) p,p'-diisocyanate diphenyl methane
- 3) Naphthalene-1,5-diisocyanate
- 4) Bi-toluylene diisocyanate
- 5) Di-anisidine diisocyanate
- 6) Paraphenylenediphenylene diisocyanate
- 7) Metaphenylenediphenylene diisocyanate
- 8) Meta xylylene diisocyanate
- 9) Benzidine diisocyanate

The quantities of diisocyanates and polyesters or polyethers when used in accordance with this invention should be close to a one-to-one molar ratio for best results. When used in this ratio, the resulting polyurethanes have good stability and may be milled and stored indefinitely. Evidence of slight cure or set up can sometimes be observed at very slight excess diisocyanate over the 1:1 molar ratio of diisocyanate to the polyester or polyether but the one-to-one molar ratio is the most desirable.

The methods of the present invention are particularly well suited for the treatment of fibres of synthetic materials such as polyhexamethylene adipamide and polyethylene terephthalate. It may also be applied to oriented fibres of polycaprolactam which is commonly called pedlon. The term "nylon" is therefore to be construed as including both polyhexamethylene adipamide and polycaprolactam.

The resin-forming materials in the treating composition are used with a resin-forming or condensation catalyst which is preferably a basic catalyst such as the hydroxides and sulfites of sodium, potassium and ammonia. The resins produced are preferably soluble in water to about 2% to 10% by weight. These resins should then polymerize or set up rapidly into an insoluble form at temperatures of about 250 to 300°F or less.

A preferred phenolic compound is resorcinol although other polyhydroxy phenols are suitable such as those having the hydroxyl groups in the benzene nucleus at a position meta with respect to each other including resorcinol and orcinol. It is preferred that the proportion of the phenolic compound in the treating solution be about 2% to 5% by weight.

A preferred aldehyde is formaldehyde although other aldehydes may be substituted for the formaldehyde in whole or in part such as acetaldehyde and furfural. It is preferred that the aldehyde be used in a slight molar excess over that actually required to react with the phenol so that all of the phenolic compound will be reacted so as to eliminate any danger of any excess phenol altering the curing step.

The condensation catalyst is preferably a basic catalyst such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, or sulfites of sodium, potassium and ammonia or mixtures thereof. The percentage of catalyst used is generally about 0.2 to 10 percent by weight based on the weight of the resin forming materials.

It is understood that the time and temperature factors relating to drying the treated fabric or curing the elastomer may be varied from that ordinarily used in the manufacture of tyres and belting in order to obtain substantial polymerization of slower reacting resin forming materials that may be used in the treating composition.

The fabric may be treated so as to apply the treating composition in any satisfactory manner such as passing the fabric or cord through a bath of resorcinol and formaldehyde, with a condensation catalyst and then passing the fabric through two doctor knives or squeeze rolls to remove the excess treating composition from the fabric and thereafter passing the fabric over a series of dryer rolls at a high enough temperature to dry the fabric and polymerize the resin. Generally the drying process

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at some stage raises the fabric temperature from about 80°C. to about 100°C. to insure a substantial polymerization of the resin-forming materials. Other methods suitable for applying the treating composition to the fabric may be used such as employing transfer rolls, spraying, brushing and the like. If desired, the cord may be dipped in a water bath before being dipped in the resorcinol-formaldehyde bath. The pre-dip of water wets the cord and tends to decrease the amount of resorcinol formaldehyde pick-up.

The drying of the treated fabric or cord may be accomplished in other ways such as carrying the treated cord by means of a belt or frame through a heated closed chamber.

When a cord treated in accordance with the present invention is dried and plied upon a compounded flexible polyurethane elastomer such as may be used advantageously in the manufacture of tyres and the whole mass is cured or vulcanized at a vulcanizing temperature so as to cure the polyurethane stock completely, the bond between the polyurethane rubber and the treated cord is found to be of a high degree. When an "H" Single Cord Adhesion Test is conducted on a fabric and polyurethane rubber bonded according to the present novel methods, adhesion between the cord and rubber, in some cases, is found even to exceed the cord strength itself.

The method of the present invention effects a high degree of adhesion between the nylon cord and polyurethane rubber in tyres and other articles.

That the method of the present invention produces a superior bond between polyurethane elastomers and nylon cords is shown by the series of tests described below:

A 0.045 gauge sheet of polyurethane rubber elastomer was made from the reaction product of about 1 mole of the polyethylene propylene adipate described above and about 1 mole of $\text{P}_\text{P}_\text{I}$ - diisocyanato - diphenyl methane compounded with carbon black. The surface of the polyurethane sheet was treated with dimethyl formamide to provide a clean surface for subsequent bonding to a fabric. Nylon cords were treated by dipping in each of the various aqueous solutions of resorcinol formaldehyde containing a catalyst as indicated in Table I.

TABLE I

Ingredients	Parts by Weight				
	A	B	C	D	E
Smooth rubber latex (75/25 butadiene/vinyl pyridine)	100	25	None	None	None
Phenolic compound (resorcinol)	11	11	11	11	11
Aldehyde (Formaldehyde)	6	6	6	6	9
Catalyst: (Sodium hydroxide)	0.3	0.3	0.3	0.3	0.3
Total Solids (Percent by weight)	20	10	5	2.5	5
Water content by weight	80	90	95	97.5	95

The treated nylon cords were dried at a temperature of 350° to 450°F for about 20 to 30 seconds. The cords were plied with the polyurethane elastomers previously described by calendering and the plied structure was further bonded by curing it for about 20 to 60 minutes at about 50 steam-pressure in test-specimen molds at an elevated temperature sufficient to vulcanize the rubber which is preferably about 250° to 350°F.

The resultant cured samples were made so as to be adaptable to the "H" Single Cord Adhesion test.

Data was taken from adhesions which were pulled at room temperature and 100°C. as shown in Table II.

TABLE II

Table of Results

"H" Adhesion — lbs.

Sample No.	Room Temperature	100° C.
A	17.2	13.8
B	19.8	15.3
C	26.5*	23.4
D	25.1	22.9
E	24.8	23.0

* Indicates that a cord break occurred before an adhesive bond break.

As seen from the Table of Results, the adhesion of polyurethane rubber to treated nylon cords in accordance with the present invention is of an unusual high degree. Unexpectedly, cord treating solutions containing an aldehyde heat hardening resin alone provides a much stronger bond between synthetic cords and polyurethane rubber than solutions containing a rubber latex.

It is important to note that at room temperature, the cord fails generally at about 26 to 28 lbs. and in one case the cord break occurred before bond failure. The "H" adhesion value of a nylon cord with no adhesive is only about 10 lbs. The excellent performance of samples at elevated temperatures is also important. As noted in Table II, samples C, D and E treated by the methods of this invention exhibit high "H" adhesion values of about 23 lbs. and even better at 100°C.

Instead of drying the cord at elevated temperatures, the cord or fabric may be dried even at room temperature or slightly above, and then subsequently vulcanized at elevated temperatures after being plied with the polyurethane elastomer.

WHAT WE CLAIM IS:—

1. In the manufacture of tyres, the process of bonding tyre cords of nylon or of polyethylene terephthalate to a saturated polyurethane elastomer by forming on the cords a

coating of an infusible insoluble resinous condensation product of an organic aldehyde and a polyhydric phenol and thereafter applying the elastomer under pressure to the cords.

2. The process according to claim 1 in which the coating comprises a resorcinol formaldehyde condensation product.

3. The process according to claim 2 which comprises dipping the cords in an aqueous solution of resorcinol and formaldehyde containing a condensation catalyst, drying the cords, calendering the cords to the elastomer and thereafter vulcanising the elastomer.

4. The process according to claim 3 in which the solution contains from $\frac{1}{2}$ to 5% by weight of the phenol.

5. The process according to any of claims 1 to 4 in which the elastomer is the product obtained by reacting approximately equimolar proportions of a linear long chain polyglycol with a polyisocyanate.

6. The process of bonding tyre cords to a polyurethane rubber substantially as herein described with reference to the Tables.

7. A rubber tyre comprising cords of a nylon or a polyethylene terephthalate whenever produced by the process according to any of the preceding claims.

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